

THE THERMO-ELECTRIC BEHAVIOR OF SILVER IN A
THERMO-ELEMENT OF THE FIRST CLASS

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THE THERMO-ELECTRIC BEHAVIOR OF SILVER IN A THERMO-ELEMENT OF THE FIRST CLASS.

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INTRODUCTORY.

THE research recorded in the following pages has for its object an investigation of the thermo-electric behavior of silver, with special reference to the more general problem of the relation of heat to electromotive force. Throughout the work, three subsidiary problems have been kept in view — namely, (*a*) an investigation of the direction of the electromotive force due to a difference of temperature; (*b*) an investigation of the relation of the electromotive force due to a given difference of concentration, to that due to a corresponding difference of absolute temperature; and (*c*) an investigation of the relation of thermo-electromotive force to the concentration of the electrolyte.

For the sake of clearness in the use of terms, the following explanatory paragraphs are given :

Two electrodes of a given metal immersed in a solution of the salt of this metal, constitute a reversible element of the simplest type. Consider the cell to be of the ordinary U-form, and let the two limbs of the cell, and also the two electrodes contained therein, be represented by the symbols *A* and *B*. Also, the cathode is that electrode *to* which the current flows in the electrolyte, or *from* which the current flows in the external circuit. A concentration cell, of the form described above, is one in which the concentration of the electrolyte in *A* differs from that in *B*; a thermo-element is one in which the concentration is the same in both limbs, but the temperature in *A* differs from that in *B*. An element of the first class is a cell in which the two electrodes are of the same metal, and are immersed in a solution of a salt of this metal.

Now, it is a well known fact that a difference of electromotive force may be established between the electrodes *A* and *B* in at least two ways. First, an electromotive force will result from a difference of concentration at *A* and *B*, the temperature on the two sides being the same; and second, an electromotive force will result from a difference of temperature at *A* and *B*, the concentration on the two sides being the same. An electromotive force due to a difference of temperature will be referred to as a thermo-electromotive force.

HISTORICAL.

As early as 1825 Walker¹ experimented on the relation of heat to electromotive force. He was followed by Faraday,² and later by Gore.³ All three in general used platinum electrodes, hence their results were vitiated by polarization effects. In the few cases in which electrodes of the same metal as the salt in solution were used, complex chemical reactions seriously interfered with definite results.

In 1880 Bouty⁴ reported a series of tests in which he used as electrodes a number of metals immersed in solutions of their own salts. For copper, zinc, cadmium, and mercury, the warm electrode was the cathode; for iron the results were very erratic; for gold the direction of the current changed for different temperatures; for silver, nickel, magnesium and aluminium the results were variable and unsatisfactory, the cold electrode, in general, being the cathode. He concluded that the electromotive force is proportional to the change in temperature and is independent of the concentration.

Carhart⁵ confirmed Bouty's results for copper and zinc, but found that the electromotive force is not independent of the concentration. His researches with reference to the change of electromotive force with change of concentration were later confirmed by Ebling,⁶ who worked on cells of the type, $\text{Cu} - \text{CuSO}_4, \text{Zn} - \text{ZnSO}_4, \text{Cd} - \text{CdSO}_4$.

¹ Pogg. Ann., 4, 327, 1825.

² Exp. Researches, Sr., 17, 225, 1932, 1840.

³ Proc. Roy. Soc., 1856, and following.

⁴ J. de Phys., 9, 1880; Comp. Rend., 90, 918, 1880.

⁵ Carhart's Primary Batteries.

⁶ Wied. Ann., 30, 130, 1887.

Nernst,¹ using mercury electrodes in a thermoelement of the type, $\text{Hg} - \text{Hg}_2\text{Cl}_2 - \text{HCl} - \text{Hg}_2\text{Cl}_2 - \text{Hg}$, found the warm electrode to be the cathode.

In 1894 Hagenbach² repeated the experiments of both Bouty and Ebling. His results for copper, zinc and cadmium agreed well with those of Ebling. In many particulars, however, his results did not agree with those of Bouty. For example, in the case of $\text{Ni} - \text{NiSO}_4$, Bouty reported that the cold electrode was the cathode. Hagenbach repeated the experiment, and reported that no definite results were attainable. He also reported that silver electrodes in solutions of silver salts gave unreliable results.

In connection with his thermo-electric theory of concentration cells, Carhart³ investigated the electromotive force of cells of the following types: $\text{Zn} - \text{ZnSO}_4 - \text{Zn}$, $\text{Zn Amal.} - \text{ZnSO}_4 - \text{Zn Amal.}$, $\text{Ni} - \text{NiSO}_4 - \text{Ni}$. He called attention to the relation between the concentration of the electrolyte and the thermo-electromotive force, and also its import when applied to the Helmholtz equation for electromotive force.

McClellan⁴ in 1903, and Meyer⁵ the following year, worked on the problem of the thermo-electromotive force of nickel nitrate. Both, however, used platinum electrodes, hence obtained unsatisfactory results due to polarization effects.

It may be noted in this connection that the Peltier effect, both at the surface of contact of a metal and a solution, and at the surface of separation of two electrolytes, has been measured by a number of investigators,⁶ who have shown that in general the same laws appear to hold as in the case of metals.

DISCUSSION OF THE PROBLEM.

The Gibbs-Helmholtz equation for electromotive force is based on fundamental principles of thermo-dynamics; the Nernst equa-

¹ Zeit. f. Phys. Chem., 4, 169, 1889.

² Wied. Ann., 53, 1894.

³ Trans. Am. Electrochem. Soc., 1, 1, 1902; 2, 123, 1902.

⁴ PHYS. REV., 17, 255, 1903.

⁵ PHYS. REV., 19, 156, 1904.

⁶ (a) Pogg. Ann., 13, 467, 1870; (b) Wied. Ann., 9, 573, 1880; (c) Ann. de Chim. et Phys., (7), 3, 83, 1894.

tion is derived from the conception of solution pressure and osmotic pressure as applied to the electrode and electrolyte of a cell. The former is, mathematically speaking, the more rigid of the two; the latter, however, lends itself, within certain limits, more readily to experimental demonstration. In the Nernst equation the electromotive force is expressed as a function of the solution pressure of the metal, the osmotic pressure of the solution, and the temperature. It assumes the application of the gas laws, and takes no account of sources of electromotive force other than those mentioned above. A general expression of this equation is as follows:

$$E = \frac{R}{Kn} \left[T_1 \log \frac{P_1}{p_1} - T_2 \log \frac{P_2}{p_2} + T_3 \frac{u-v}{u+v} \log \frac{p_1}{p_2} \right]. \quad (1)$$

E represents the resultant electromotive force of the cell; T , absolute temperature; R , the gas constant; K , 96,540 coulombs; n , valence; P , solution pressure of the metal; p , osmotic pressure of the solution; u and v , migration velocities of the ions.

When $P_1 = P_2$, and $T_1 = T_2 = T_3$, equation (1) may be written

$$E = \frac{RT}{Kn} \left[\frac{2v}{u+v} \right] \log \frac{C_1}{C_2}, \quad (2)$$

in which the ratio of concentrations, C_1/C_2 , is set equal to the ratio of osmotic pressures, p_1/p_2 .

Nernst has proved that under certain conditions, as in the case of $\text{Ag} - \text{AgNO}_3$ concentration cell, the calculated values, obtained by means of equation (2), agree remarkably well with the observed values.

Now, the question arises, how far can this proof be extended under other conditions of the variables T and p ? That is to say, how far, for example, will the conception of solution pressure and osmotic pressure, as applied to the concentration cell, explain the phenomena of a thermo-element of the first class?

The results of investigation thus far, with respect to the relation of heat to electromotive force, may be collected under three heads as follows: First, work done with polarizable electrodes; second, work done with unpolarizable electrodes in cells of the second class — that is, cells of the type, $\text{Hg} - \text{Hg}_2\text{Cl}_2 - \text{HCl} - \text{Hg}_2\text{Cl}_2 - \text{Hg}$;

and third, work done with unpolarizable electrodes in the cells of the first class — namely, of the type, $\text{Zn} - \text{ZnSO}_4 - \text{Zn}$. It is to phenomena connected with cells of the last named group that this paper invites attention, since in cells of this class are found the simplest possible conditions and the fewest disturbing factors.

The writer is perfectly well aware that the mere tabulation of data does not offer a solution to the problem. Before such data can be of much value we must have pretty definite information regarding the physical condition of the electrodes, the nature of the electrolyte, and what occurs when these component parts of the cell are combined. If, for example, the electrodes are oxidized, or contain occluded gases, or become polarized, variable and unsatisfactory results will necessarily follow. Or, again, if in the case of the electrolyte, unknown and complex physical or chemical changes occur in the process of solution, little can be expected in the way of definite results.

Assuming now that the above-named conditions can be fairly well satisfied, let us consider for a moment the relation of E to the variables T and p (absolute temperature and osmotic pressure). If in the U-shaped cell previously mentioned the electrolyte be of uniform concentration, and the electrode A be brought to a temperature higher than B , then p in limb A will be greater than that in limb B , since the osmotic pressure varies as the absolute temperature. Then, assuming that the solution pressure, P , does not change, and assuming also that no other factors enter in, the resulting electromotive force will be directed *in the electrolyte* from the cold electrode to the warm; that is to say, the warm electrode will be the cathode. If, however, the cold electrode prove to be the cathode, then it will be necessary to revise our assumptions, or look for other factors as a source of electromotive force, in addition to those already named.

Also, since E is a function of p , and p in turn is a function of both T and C , it is possible to vary p , and therefore E , by varying either the absolute temperature T , or the concentration C .

Now, if the conditions be chosen such that T_1 (equation 1) be equal to T_2 , and p be varied through a series of values, y_1, y_2 , etc., by making C_1 greater or less than C_2 , a resultant electromotive force, E' ,

will be observed in accordance with the well-known laws of the concentration cell. Suppose, further, that C_1 be made to equal C_2 (equation 2) and p be varied now through a calculated series of values, p_1, p_2 , etc., as above, by making T_1 greater or less than T_2 , again there will result an electromotive force, say E'' . How will E'' compare with E' , previously obtained? Theoretically, the two values should be the same. In case a difference in value between E' and E'' be found, and such difference be greater than that due to experimental error, then again we must revise our assumptions, or look for some additional factor as a source of electromotive force.

Then, to summarize, in considering an element of the first class in connection with the subject of the relation of heat to electromotive force, three important questions arise. First, do all metals immersed in solutions of their own salts, under conditions as described, give a current through the electrolyte from the cold to the warm portion — that is, is the warm electrode the cathode? Second, how does the electromotive force resulting from osmotic pressure changes, due to a given difference in concentration, compare with the electromotive force resulting from osmotic pressure changes, due to a corresponding difference in absolute temperature? And third, in a thermo-element, what is the relation between the concentration of the electrolyte and the resulting thermo-electromotive force? In other words, to summarize all three questions, under varying conditions of the temperature, will the factors of solution pressure and osmotic pressure account for the observed electromotive force?

The answer to these questions involves the working out of a large and complex problem, the solution of which requires much more extended research than comes within the limits set for this paper. The following investigation has to do mainly with the thermo-electric behavior of silver, and has been prosecuted with the hope that some further light may be thrown on the general problem of the relation of heat to electromotive force.

APPARATUS.

The following is a brief and general description of the apparatus used, special pieces, such as electrodes, etc., being described later in connection with the experiments.

Two thermostats were employed, and are shown in outline in Figs. 1 and 3. Temperature measurements were made by means of Beckmann thermometers, reading directly to hundredths of a degree.

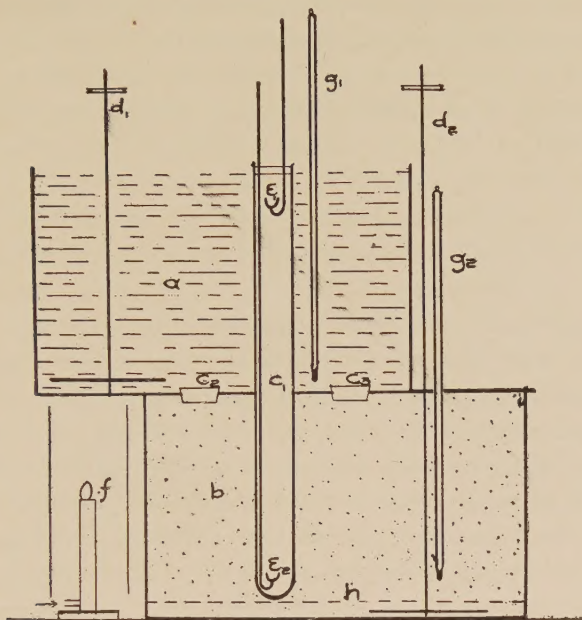


Fig. 1.

The temperature in the warm bath was held constant to within a few hundredths of a degree by means of large toluene-mercury regulators. In the thermostat shown in Fig. 1, the ice bath was in the lower chamber; in the case of that shown in Fig. 3, the ice bath consisted of a large Dewar flask enclosed in a jacket of building felt. In the thermostat shown in Fig. 1, a stirrer was used in both chambers; in that shown in Fig. 3, a stirrer was used only in the warm bath.

Measurements of electromotive force were made by means of an Otto Wolff potentiometer which reads directly to 0.00001 volt. A Leeds and Northrup galvanometer was employed of such sensitiveness that a change of 0.00001 volt gave a deflection of one scale part, at a distance of ten feet. The electromotive force to be measured was balanced against that of a standard cadmium cell.

EXPERIMENTS AND RESULTS.

A preliminary test was made with reference to the direction of the electromotive force of a number of metals when immersed in solutions of their own salts. A large H-formed cell was employed, the cross-tube of which contained a stop-cock. During the test, one leg of the cell was kept in a 25° bath; the other, in ice. The following types of reversible cells were used: $\text{Zn} - \text{ZnSO}_4 - \text{Zn}$; $\text{Cd} - \text{CdSO}_4 - \text{Cd}$; $\text{Cd Amal.} - \text{CdSO}_4 - \text{Cd Amal.}$; $\text{Hg} - \text{HgNO}_3 - \text{Hg}$; $\text{Ag} - \text{AgNO}_3 - \text{Ag}$.

In the case of zinc, cadmium, cadmium amalgam and mercury, the warm electrode was the cathode; in the case of silver, the cold electrode was the cathode.

A more pretentious piece of apparatus was now constructed, and a more thorough investigation of the direction of the electromotive force of silver undertaken. Fig. 1 represents in outline the containing baths, cells, and auxiliary apparatus. The warm bath (*a*) was kept at a temperature of 25° ; the cold bath (*b*) about zero. Cell (*c*₁) consisted of a cylindrical glass tube 60 cm. in length, and about 5 cm. in diameter. Two stirrers were provided, *d*₁ and *d*₂, the latter working in the cold water below the ice. The flame (*f*) was controlled by a regulator not shown in the cut. It was easily possible to hold the temperature constant in either bath to within a few hundredths of a degree. It may be well to remark here that this particular piece of apparatus was devised with two objects in view — namely, (*a*) the investigation herein described, and (*b*) an investigation of the so-called Soret phenomenon, for the accomplishment of which the apparatus is admirably adapted. Openings between the chambers (*a*) and (*b*), Fig. 1, were provided for five cells similar to (*c*₁), three such being shown in the cut.

The electrodes (*E*₁) and (*E*₂) deserve special mention. At the beginning of the work great difficulty was experienced in getting electrodes that would give anything like zero initial values. What was required were electrodes that would give zero readings to nearly the fifth decimal place, and second, electrodes that would give reproducible and constant values for several days or weeks. As already stated, unusual difficulties were met with in attempting to fulfill these conditions. Electrodes prepared from the same piece

of metal, under apparently the same conditions, would sometimes give an initial electromotive force of as high as 0.003 to 0.005 volt. And again, after electrodes were obtained that would give the required initial reading, it was found that they would not remain constant for any length of time, going now to positive values, and again to negative, in a most hopeless and discouraging manner. In view of the difficulties just mentioned, it is not at all surprising that Bouty and Hagenbach spoke of silver as "variable" and "unreliable."

The first difficulty encountered was in sealing the electrode to the glass supporting tube. In a few cases it was possible to seal fine silver wire directly into the glass, but in most cases this failed. After a test extending over a period of two or three months, all methods of sealing in with wax in any form were abandoned. Such electrodes in a solution of silver nitrate invariably "broke down" — that is, they eventually gave erratic and variable results, due to the action of the solution upon the wax. Electrodes prepared by depositing, electrolytically, silver on clean platinum spirals gave fairly good results, so far as constancy was concerned, but it was found that two sets of electrodes prepared in exactly the same manner, and immersed in the same solution would often give widely different results.

The electrodes finally made use of were prepared after the following manner: From the purest obtainable chemicals, silver chloride was precipitated. The chloride was filtered out, washed and then dissolved in ammonium hydroxide, and from this solution the silver was precipitated by means of pure electrolytic copper. The precipitated silver was now digested in excess of ammonia, after which it was thoroughly washed. The final product consisted of a fine grayish powder, which will be referred to hereafter as "precipitated silver." The complete form of this electrode is shown in Fig. 2. The precipitated silver, just described, was placed in the cup (*j*). A long silver wire (*m*) was fused to a short platinum wire (*k*) at (*l*). The platinum wire, in turn, was fused through the glass as shown, the point which protruded into the cup (*j*) being silver plated, thus making electrical contact with the metal of the electrode proper. In one case, hereafter mentioned, no platinum

wire was used, the silver wire (m) being fused through the cup at (j). With such electrodes, except that the form was modified later on, all the results recorded with reference to silver were obtained. It was found possible to obtain zero initial readings to nearly the fifth decimal place, and further, not only did different sets of electrodes give concordant results, but the values showed remarkable constancy over a relatively long period of time.

Nothing new is claimed for the above method for the preparation of silver, or for the use of finely divided metal as an electrode.¹ The details are given because, of the many methods suggested, the foregoing gave the most satisfactory results.

Cell (c) (Fig. 1) was now filled with a tenth normal solution of silver nitrate. Both electrodes (e_1) and (e_2), were placed near the top of the cell (Tem. 25°), and the initial electromotive force observed. Electrode (e_2) was then lowered to the bottom of the cell (Tem. near 0°), and observations were taken over a period of twenty days.

The object of this test was threefold, namely (a) to note the direction, (b) the constancy, and (c) the conditions attending the resulting electromotive force over a considerable period of time.

The results of the test are embodied in Table I.

In considering Table I., it is to be noted that the cold electrode remained the cathode throughout the experiment, and that the electromotive force was remarkably constant. Further the elimination of oxygen from the electrolyte by exhaustion, and then saturating the solution with nitrogen, seemed to produce no notable change in the values observed. After exchanging the electrodes, the electromotive force was 0.00030 volt higher than before the change. This small difference might be accounted for by the fact that at the close of the experiment it was found that one of the glass tubes of the electrodes was slightly cracked, allowing a little of the solution to come in contact with the silver wire (m) (Fig. 2).

It was now thought desirable to repeat the experiment recorded in Table I., and to extend the test to other metals. The object here was to compare silver, mercury, and cadmium amalgam under similar conditions, and also to see if the "Soret effect" entered into the problem. By the "Soret effect" is meant the production of a

¹ Richards and Lewis in Zeit. f. Phys. Chem., 28, 8.

TABLE I.

Date.	$T_1 - T_2$	E.M.F.	Notes.
Feb. 25, 8 A. M.	0.0	0.00006	Initial condition of electrodes. Bath at 25°. Electrode <i>A</i> at top. Temperature = 25°. Electrode <i>B</i> at bottom. Temperature = 0°. Cold electrode cathode (+).
" 25, 11 "	24	966	
" 25, 8 P. M.	23.75	961	
" 26, 8 "	23.5	960	
" 27, 8 A. M.	23.9	963	
" 27, 12 "	23.7	965	
" 28.	23.5	966	
March 1.	23.3	967	
" 2, 8 A. M.	23.5	965	
" 2, 1 P. M.	23.6	968	
" 2, 9 "	23.7	966	
" 3.	23.6	964	The electrodes were now exchanged — electrode <i>A</i> ' was put at bottom; <i>B</i> at top. <i>A</i> changed from — to +; that is, the cold electrode again became the cathode.
" 3.	23.7	0.00130	
" 4.	23.6	1071	
" 5.	23.8	1045	
" 6.	23.6	1022	
" 7.	23.7	1002	
" 8.	23.7	977	Had trouble here with motor; water in bath not well stirred.
" 9.	23.6	977	
" 10.	23.7	975	
" 10, 2 P. M.	23.8	990	From this time on the solution in the cell was saturated with pure nitrogen.
" 10, 9 "	23.7	993	
" 11.	23.6	998	
" 12.	24.5	980	
" 13.	23.6	991	
" 14.	23.8	992	
" 16.	23.7	995	
" 17.	23.9	998	

difference of concentration in the cell due to the difference in temperature. The solution at the top of the cell (c_1), Fig. 1, was at a temperature 25° higher than that at the bottom. This difference of temperature would produce, at the outset, a corresponding difference of osmotic pressure, the greater pressure being at the top. According to the theories embodied in an explanation of the Soret phenomenon,¹ however, equilibrium in the cell would eventually be

¹ Ann. de Chim. et Phys. (5), 22, 293, 1881.

established by an osmotic pressure at the bottom of the cell (the cold portion) due to an increase of concentration, equal to that at the top, due to the increase of temperature. In other words when the contents of the cell came to equilibrium, the solution should show an increase of concentration at the bottom (the cold portion) proportioned to the difference of absolute temperature between the two extremities of the cell.

Two new cells (c_2 and c_3), Fig. 1, were now put into the bath in a manner similar to that of c_1 . The three cells were of the following types: Ag — AgNO₃; Cd Amal. — CdSO₄; Hg — HgNO₃ + HNO₃.

The silver electrodes were similar to those described in connection with Table I. In this case no platinum wire was used in the construction of the electrode, the silver wires being fused into the glass at (k), Fig. 2. Long wires were used to avoid any possibility of a thermo-electromotive force of metallic contact.

The cadmium amalgam electrodes were, in outline, similar to that shown in Fig. 2. In this case, however, the cup (j) was filled with twelve and a half per cent. cadmium amalgam. The tube (i) was also filled with amalgam, which made electrical contact with (j) by means of a short platinum wire (k). The platinum wire was so short that there was no possibility of a resultant electromotive force of metallic contact, since in both electrodes there could be no difference of temperature at the ends of the wire.

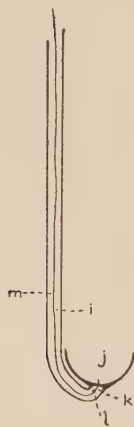


Fig. 2.

The mercury electrodes were prepared in a similar manner.

In the case of the electrolyte, a tenth normal solution was used in each of the cells. Just enough nitric acid was added to the mercury cell to hold the mercurous nitrate in solution.

After the experiment had been in operation seven days, analyses for concentration changes at the electrodes were made several times a day. By means of a long capillary pipette a small quantity of the electrolyte of a given cell was drawn off from the cold and the warm portions, and tested for concentration changes by conductivity methods.

A record of the experiment follows in Table II.

TABLE II.

Date.	$T_1 - T_2$	$\overset{Ag}{\text{Cold El.}}$ +	$\overset{Cd\ Amal.}{\text{Hot El.}}$ +	$\overset{Hg}{\text{Hot El.}}$ +	Notes.
May 20	0.0	0.00008	0.00012	0.00000	Both electrodes at 30°.
" "	29.95	1105	1184	340	
" 21	30.00	1234	1157	338	
" "	30.00	1264	1162	350	
" 22	29.97	1270	1163	352	
" 23	30.02	1278	1173	363	
" 24	30.03	1278	1176	366	
" 25	30.01	1279	1174	364	
" 26	30.00	1284	1168	368	
" 27	29.90	1276	1179	368	
" 28	29.92	1266	1183	374	Analysis was begun here.
" 29	29.97	1278	1194	372	
" 30	30.00	1281	1195	384	

Analyses during the progress of the experiment recorded in Table II. showed no changes of concentration at the electrodes — in other words, showed no evidence of the Soret phenomena. This was probably due partly to the length of cell used (60 cm.), and also to the fact that sufficient time had not elapsed for such a change to make itself manifest. A further investigation of the Soret phenomenon will be made with the apparatus just described and shown in outline by Fig. I.

In the case of silver, the cold electrode remained the cathode. For cadmium and mercury the warm electrode was the cathode.

Silver and cadmium gave remarkably constant values.

A careful investigation was now begun with reference to the physical character of the electrode in the case of silver. The test was qualitative in character and included cells of the types, $\text{Ag} - \text{AgNO}_3$; $\text{Ag} - \text{AgClO}_4$.

The large H-form cell, used in the preliminary tests, was employed. One leg was kept at a temperature of 25°; the other at the temperature of the ice bath. After each test the electrodes were reversed with respect to the warm and the cold sides of the cell and new readings taken.

The silver wire described in the tests was prepared as follows: Silver was deposited electrolytically, and the product was fused and run into sticks, which in turn were drawn into wire. This wire when freshly drawn was very brittle, but when slightly annealed became very soft and pliable. The other forms used were (a) silver deposited on platinum, (b) silver cleaned in dilute nitric acid, (c) precipitated silver, as previously described.

The conditions, under which the tests were carried out, and the results are given in Table III.

TABLE III.

Test No.	Condition of Electrode.	Result.
1	Freshly drawn silver wire—Unannealed—Brightly polished.	Cold electrode, cathode.
2	Freshly drawn silver wire—Annealed in Bunsen flame—Brightly polished.	“ “
3	Freshly drawn silver wire—Annealed in an atmosphere of pure nitrogen by means of an electric current.	“ “
4	Freshly drawn silver wire—Cleaned in dilute nitric acid.	“ “
5	Silver deposited from tenth normal solution of silver nitrate on platinum spiral.	“ “
6	Silver deposited on platinum spiral from standard cyanide silver-plating solution.	“ “
7	Heavy deposit of silver, prepared as in (5), and cleaned in 50 per cent. solution of nitric acid.	“ “
8	Precipitated silver, as previously described.	“ “

It thus appears from the preceding tables that silver in a neutral solution of AgNO_3 or AgClO_4 , as a thermo-element, gives for a difference of temperature between 0° and 30° , an electromotive force directed in an opposite sense to that of zinc, copper, cadmium and mercury.

The second part of the investigation was now taken up, namely, an investigation of the relation between concentration changes and corresponding temperature changes, in the production of electromotive force. As a preliminary step, a few tests were made with reference to the temperature coefficient of a concentration cell of the type, $\text{Ag} - \text{AgNO}_3 - \text{Ag}$. According to the formula used in

the calculation of the electromotive force of such a cell, the E.M.F. should vary directly as the absolute temperature, the difference in concentration remaining constant and the temperature being the same on both sides.

The H-form of cell, previously mentioned, was employed, and precipitated silver was again used as electrodes. No attempt was made to carry the experiment to any great length, it being required merely to show that under the conditions assigned, no abnormal changes occurred.

Summary of results given in Table IV.

TABLE IV.

Cell No.	C_1/C_2	Cond. of Electrodes.	Calc. E.M.F.	Obs. E.M.F.
1	5.260	Both electrodes at 30°.	0.04564	0.04500
1	"	Cell placed in ice bath. $T. = 0.06^\circ$.	0.04149	0.04000
1	"	Cell again placed in 30° bath.	0.04564	0.04540
1	"	Cell again at 0.06°.	0.04149	0.04174
2	1.596	Temp. = 30°.	0.01291	0.01310
2	"	Temp. = 1.25°.	0.01174	0.01223
3	1.670	Temp. = 30°.	0.01408	0.01432
3	"	Temp. = 0.06°.	0.01282	0.01260

The apparatus used in this part of the work is shown in Figs. 3 and 4. The cell employed was of the three-legged form, two limbs (A_1 and A_2) being kept in the warm bath, the remaining limb (A_3) in the ice bath. A_1 , A_2 and A_3 were connected by means of siphons each of which contained a stop-cock.

The method of procedure was as follows: A neutral tenth normal solution of silver nitrate was put into all three cells. Cells A_1 and A_2 combined were designed to act as a concentration element;

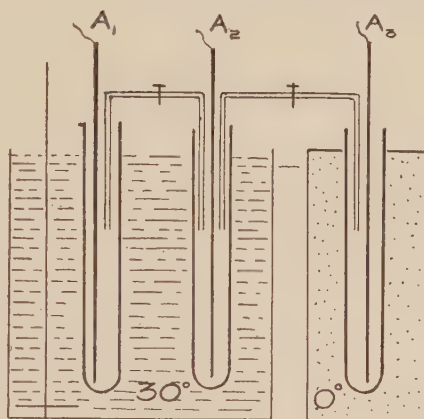


Fig. 3.

cells A_2 and A_3 to act as a thermo-element. Due to the difference of temperature between A_2 and A_3 there resulted an electro-

motive force, the ratio of the absolute temperatures of the two sides being $303 : 273$, or 1.11 . With this combination the cold electrode was as usual the cathode. The next step was to vary the concentration in A_1 through a series of values, thus giving a series of E.M.F. readings due to the difference of concentration between A_1 and A_2 . The object was to find what concentration ratio was required to produce an electromotive force equal to that due to an absolute temperature ratio of 1.11 .

In the preliminary tests the electrodes used were prepared by electrolytically depositing silver upon platinum spirals. The results obtained with this form of electrode were not entirely satisfactory.

In the final test in this case, and in all subsequent tests, the precipitated silver electrodes were used to the exclusion of all others.

The form of electrode used in the final test is shown in Fig. 4. A long silver wire (p) was fused to a very short platinum wire (r), which in turn was sealed into the lower portion of the tube (t) in such a manner that the point (s) projected out of the side of the tube a few millimeters from the end. This was to prevent the silver-plated point (s) from being injured on the bottom of the cell.

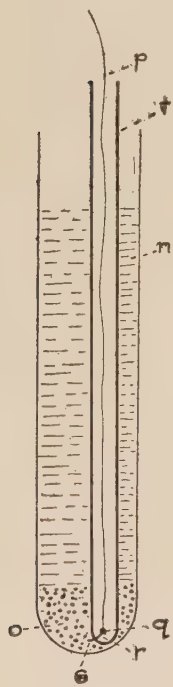


Fig. 4.

To set up the cell, precipitated silver to the depth of one or two centimeters was put into each limb (A_1 , A_2 and A_3). A given solution of silver nitrate was then added *and the contents of each cell thoroughly shaken*. The tubes containing the conducting silver wires were now put into the cell, as shown in Fig. 4, the silvered point (s) making electrical contact with the precipitated silver. The cells were now put into their respective baths and connected by means of the two siphons, as shown in Fig. 3.

A thermo-electromotive force at once resulted between A_2 and A_3 , due to a difference of temperature of 30° . A_1 and A_2 , on the other hand, being of the same temperature and concentration, were

in equilibrium to begin with. Now, as in the preceding test, the concentration in A_1 was varied through a series of values by the following method: After each reading the stop-cock between A_1 and A_2 was closed, and A_1 was taken from the bath. A small quantity of the electrolyte of limb A_1 was removed by means of a pipette, and a corresponding amount of water was added. The cell was then thoroughly shaken, the special form of electrode just described making this operation possible. This agitation of the electrode is quite necessary when it is desired to vary the concentration of the electrolyte through a series of values. Cell A_1 was now returned to its former position and allowed to come to the temperature of the bath.

The conductivity of the electrolyte in A_2 was taken once for all; that in A_1 was taken after each dilution. From this data the relative concentrations in A_1 and A_2 were obtained. The ratio $C_1 : C_2$, as used in the following table, represents a ratio of molecular conductivities. For each variation of the concentration in A_1 the value of the resulting electromotive force between A_1 and A_2 was calculated by means of equation (2), the data for the values of u and v being obtained from the Kohlrausch and Holborn tables. The object here of comparing the observed with the calculated values was to see how closely, under the conditions, the gas laws applied. In making the solutions described above, water prepared for conductivity purposes was used.

For tabulation of results of the foregoing tests see Table V.

TABLE V.

Comparison of the electromotive force due to a given difference of absolute temperature, with that due to a corresponding difference of concentration. For outline of cell, see Figs. 3 and 4.

C_1/C_2	T_1/T_2	Obs. E.M.F.	Calc. E.M.F.	C_1/C_2	T_1/T_2	Obs. E.M.F.
1.114	1	0.00284	0 00291	1	1.11	0.01408
1.388	1	.00813	.00910	1	1.11	0.01408
1.533	1	.01093	.01174	1	1.11	0.01408
1.710	1	.01360	.01475	1	1.11	0.01408
1.883	1	.01615	.01740	1	1.11	0.01408

It will be noted in connection with Table V., first, that the observed values agree fairly well with the calculated values, the difference

always being in the right direction; and, second, that the electromotive force due to a difference of absolute temperature represented by the ratio 1.11 is more than five times as great as that due to a corresponding difference of concentration.

Certain results obtained with the cells just described led the writer to suspect that the thermo-electromotive force in the case of silver is a certain function of the concentration of the electrolyte, as well as of the temperature. A preliminary test was made with reference to this subject. The cell used consisted of the A_1 and A_2 limbs as shown in Fig. 3. A_1 was kept at a temperature of 30° ; A_2 at 0° , or thereabouts. A solution of a given concentration was placed in the cell, after which both electrodes were thoroughly agitated. The limbs of the cell were adjusted in their respective baths, and after the electromotive force had risen to a constant value, a reading was taken. The operation was then repeated with a different concentration. The thermo-electromotive force decreased with an increase of concentration of the electrolyte, as shown by Table VI., and also by Curve I., Fig. 5, which was plotted from the values of this table.

Later the test was repeated, great care being exercised in the preparation of the electrodes. A sufficiently large quantity of the precipitated silver was used to allow for a series of tests extending over that portion of Curve I., Fig. 5, which showed the most marked change of electromotive force. The precipitated silver was thoroughly washed, and dried at a temperature of about 50° . The method of procedure was as follows: Precipitated silver to the depth of one to two centimeters was placed in the bottom of each limb of the cell (A_2 and A_3 , Fig. 3). A solution of AgNO_3 of a given concentration was then poured into the limbs A_2 and A_3 until each was about two thirds full. The contents of each limb was then thoroughly shaken, after which the conducting tubes (t) were put in place, as shown in Fig. 4. The powdered silver, which had been thoroughly incorporated with the solution in the process of shaking, quickly settled to the bottom of the tube. The two limbs were now connected by means of the siphon (Fig. 3) and the cell was then placed in position in the bath, one limb being at 25° and

the other at 0° . When the thermo-electromotive force came to a constant value a record was made.

After the test, the solution was poured out of the cell, and the precipitated silver composing the electrodes was removed. A *new portion* of the silver originally prepared was then placed in the cell, a solution of a different concentration added, and the process was repeated exactly as described above. Thus in each test practically new electrodes were employed. Three separate tests were made, each including the following concentrations: $n/80$, $n/40$, $n/20$, $n/10$. One test made with an $n/160$ solution showed very little increase in value over that of the $n/80$ solution; likewise, an $n/5$ solution gave a value only slightly below that of the $n/10$ solution. The values obtained by the three series of tests agree remarkably well with each other, as shown by Table VII. Curve II., Fig. 5, is plotted from the mean value column of this table.

TABLE VI.

Conc.	Cell A_1A_2 (Fig. 3).				Cell A_2A_3 (Fig. 3).	
	C_1/C_2	T_1/T_2	Obs. E.M.F.	Calc. E.M.F.	T_1-T_2	Obs. E.M.F.
$n/10$	1.064	30/30	0.00165	0.00170	30°	0.01253
$n/20$	1.200	30/30	507	501	30	1450
$n/40$	1.215	30/30	513	530	30	1720
$n/60$					30	1823
$n/80$					30	1850
$n/100$					30	1864

TABLE VII.

Conc.	T_1-T_2	Test 1.	Test 2.	Test 3.	Mean E.M.F.
$n/80$	25°	0.01480	0.01450	0.01440	0.01457
$n/40$	25	0.01354	0.01370	0.01330	0.01351
$n/20$	25	0.01260	0.01230	0.01252	0.01246
$n/10$	25	0.01106	0.01106	0.01140	0.01127

Curves I. and II. (Fig. 5) show a fairly good agreement. It must be kept in mind that the values represented by Curve I. are due to a difference of temperature between the two limbs of the cell of 30° ; while those represented by Curve II., are due to a difference

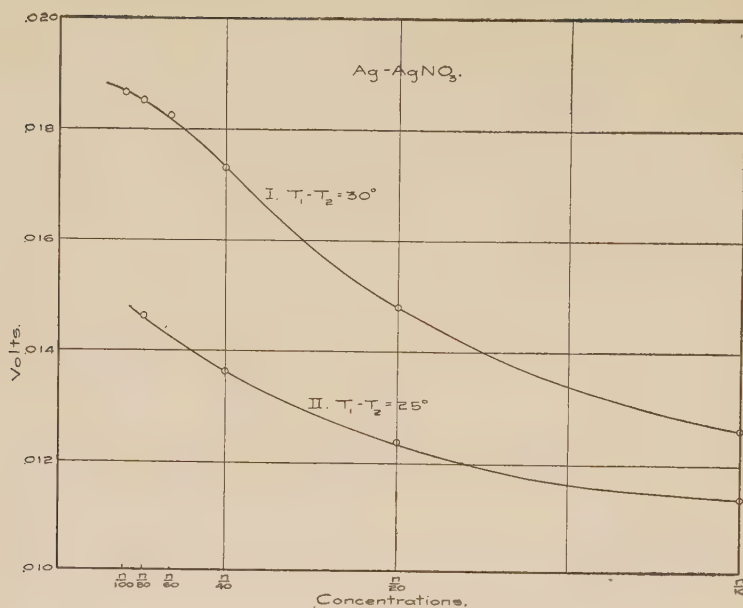


Fig. 5.

of 25° . Both indicate a maximum decrease of thermo-electromotive force between the values of one eightieth and one tenth normal.

Similar concentration curves for zinc sulphate and nickel sulphate show an *increase* of thermo-electromotive force with an increase of concentration. Such a curve for $\text{Zn} - \text{ZnSO}_4$, prepared in 1902

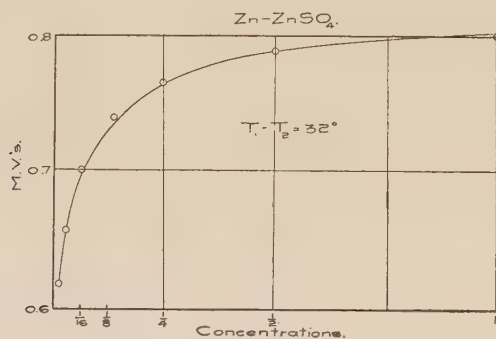


Fig. 6.

by Professor H. S. Carhart,¹ and used in the present case through his courtesy, is shown in Fig. 6. It will be noted that the curve

¹ Trans. Am. Electrochem. Soc., 2, 123, 1902.

for silver differs from that of zinc not only in direction but also in general form. This latter difference, however, is due to the portion of the respective curves chosen in plotting, and is not an intrinsic difference. The important point of the comparison lies in the difference of direction of the two curves.

SUMMARY.

In a thermo-element of the first class, in the case of zinc, copper, cadmium and mercury, the warm electrode is the cathode. In the case of silver, on the other hand, the cold electrode is the cathode. The tests to which silver was subjected indicate that this phenomenon is not due to some peculiar property of a special electrode, since many different forms and conditions of the metal were used, and always with the same result. Cells from which the air had been thoroughly removed gave results in accord with those noted; indeed, the removal of air did not appear to affect the resulting electromotive force, either in direction or magnitude. And further, not only was the thermo-electromotive force due to a difference of 25° to 30° constant during a relatively long period of time, but also the electrodes employed gave no evidence of being changed in any respect by this difference of temperature. For example, two electrodes, prepared as described, gave, when at the same temperature, an initial reading of zero to nearly the fifth decimal place. They were then subjected to a difference of temperature of 25° for ten days, after which they were brought back to the initial condition, when both electrodes again gave practically a zero reading.

In the second place, in the case of silver, the resultant electromotive force, due to a given difference of absolute temperature, is more than five times as great as the computed osmotic pressure changes would require. Table V. shows that with a given solution, a difference of concentration represented by the ratio $C_1 : C_2$ of 1.114 gave an electromotive force of 0.00284 volt, the calculated value being 0.00291 volt; while a corresponding ratio difference of absolute temperature gave an electromotive force of 0.01408 volt, a value five times as great. When we recall that this thermo-electromotive force is directed, in the external circuit, from the cold electrode to the warm, and that no account is taken of a diminution of

ionic concentration on the cold side, due to a reduction of temperature, the result appears all the more remarkable. Theoretically, from a consideration of the increase of osmotic pressure with increase of temperature, as well as the increase of ionic concentration at the warm electrode (so far as these two factors can be considered apart from one another) we should expect to find the thermo-electromotive force of silver directed in the opposite sense; and also, we should expect to find the electromotive force due to a ratio $C_1 : C_2$ of 1.114 very nearly equal in value to the electromotive force due to a ratio $T_1 : T_2$ of 1.11. The fact that in the latter case the value is five times as great as in the former is highly suggestive that there are other factors entering into the problem besides those of osmotic pressure and solution pressure.

And finally, silver shows an anomalous change of thermo-electromotive force with change of concentration. An increase of concentration in the case of zinc, copper and cadmium gives an increase of electromotive force. In the case of silver, the reverse is true.

CONCLUSION.

The prime object of the research herein recorded was the collection and coördination of the facts bearing on the thermo-electric behavior of silver, and therefore a record of the investigation practically closes with the statements of the brief summary just given. However, while a discussion of the theories relating to the subject does not properly come within the province of the present paper, yet it will not be out of place to call attention briefly in closing to certain assumptions which suggest themselves as applicable in the explanation of the phenomena observed.

The thermo-electric behavior of silver may be explained for example, in terms of solution pressure and osmotic pressure, on the assumption that the solution pressure of the metal increases, much more rapidly with increase of temperature, than the osmotic pressure of the solution. It must be noted in this connection, however, that it will require a very large increase of solution pressure to account for the outstanding observed electromotive force. It will also be necessary to make the additional assumption that the solution pressure is a function of the concentration, as well as of the tem-

perature. And it must be noted further, that when we have made these assumptions explain the thermo-electric behavior of silver, we meet with serious difficulties in applying the same general explanation to other metals, such as zinc, or cadmium, in which cases the thermo-electromotive force is directed in the opposite sense.

Again, a provisional explanation may be given on the assumption that certain thermo-chemical changes occur in the electrolyte, affecting the degree of dissociation of the salt in solution by the formation of new compounds, as for example, the products of hydrolysis.

In the third place, the phenomena observed with respect to silver may be due to the surface conditions of the electrodes used. For example, if the electrode were covered with a film of oxide, which is assumed to undergo a change more readily on the warm side of the cell than on the cold, there would undoubtedly be established conditions favorable for the production of an electromotive force.

And, to conclude, the peculiar thermo-electric behavior of silver may be explained by applying the assumptions embodied in the Carhart thermo-electric theory of concentration cells—namely, that there is a thermo-electromotive force between a metal and its salt analogous to that between two different metals, and that this thermo-electromotive force is a function of both the temperature and the concentration; and further, that the direction of the thermo-electromotive force, from the metal to the solution or vice versa, depends upon the nature of the metal composing the electrode. The assumptions in this case take no account of forces operating to produce such an electromotive force other than the energy changes which are due to differences of temperature, and which operate in accordance with the laws of thermo-dynamics. These assumptions give an explanation in accordance with the facts; they offer, however, no clue to the mechanism by which the thermo-electromotive force is brought about.

Whatever may prove to be the true explanation of the thermo-electric behavior of silver, certain it is that much remains to be done before very definite statements can be made with reference to this subject or to the more general problem of the relation of heat to electromotive force.

It is planned to continue the present research, dealing with the subject of the thermo-electric behavior of silver over a greater range of temperature than that touched upon in the present case, and also to investigate further the relation of oxidation to thermo-electromotive force.

In conclusion the writer wishes to acknowledge his indebtedness for the loan of a number of important pieces of apparatus by the department of physical chemistry of the University of Michigan, in which department the major portion of the work was done ; and to express his appreciation of the interest shown in the work by Prof. H. S. Carhart, of the department of physics, under whose direction the investigation was carried on.

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